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Description

The present invention relates to a method and apparatus (individual and collective protection filters) for removal of cyanogen chloride from an air stream containing cyanogen chloride. More particularly, the present invention is directed to an activated charcoal or carbon filter which is especially effective in removing cyanogen chloride from the air.

The use of activated carbon or charcoal which has been impregnated with metals and metal compounds as a filter to remove toxic gases has long been known. during both World Wars I and II, gas masks containing activated charcoal impregnated with copper and copper oxides were used to remove hydrogen cyanide. More recently, combinations of copper, silver and chromium have been employed with activated charcoal to remove such toxic agents as hydrogen cyanide and cyanogen chloride. The copper impregnated charcoal was called whetlerite, after C. Whetzel was instrumental in its development.

Military air filters have employed activated carbon impregnated with various compounds which are effective in removing specific toxic gases not readily controlled by carbon alone. In the U.S.A., a chromium catalyst, formed in situ on the carbon has been effectively used against the vapor cyanogen chloride. Use of this catalyst has, however, led to a number of problems.

1. The catalyst looses effectiveness when "aged" under certain conditions of humidity and temperature.
2. Conditions required to form the catalyst including carbon type and processing methods are critical and may be hard to achieve.
3. Chromium is carcinogenic and a potential hazard if carbon dust is inhaled.

Over the years a number of modified compositions have been tried which tend to improve the aging characteristics of the filter with respect to cyanogen chloride removal. These have been based on addition of organic amines to the chromium impregnated product. While a number of different types of amine compounds have been tested, the most effective has been triethylenediamine (TEDA). In the last 10 years the British Military has employed TEDA in combination with chromium salts to augment cyanogen chloride removal by their gas masks.

A search of the prior art has uncovered patents which disclose a variety of agents for enhancing the effectiveness of activated carbon for the selective sorption of gases.

U.S. 4,212,852 to Albe et al. discloses a method for using activated carbon having supported thereon metal compound of vanadium, molybdenum or tungsten to deodorize gases containing ammonia, amides and/or hydrogen sulfide.

U.S. 4,111,833 to Evans discloses activated charcoal impregnated with triethylenediamine and a mixture of iodine and potassium to remove iodine from a nuclear reactor effluent stream.

U.S. 4,040,802 to Deitz et al. discloses activated charcoal impregnated with a tertiary amine, such as triethylenediamine and iodine or bromine to remove methyl iodine from a nuclear reactor effluent stream.

U.S. 3,739,550 to Martin et al. discloses activated carbon impregnated with a mixed catalyst which includes a vanadium compound and at least one compound of potassium, lithium or barium to desulfurize carbon dioxide containing waste gases.

British Patent 1,123,822 discloses activated charcoal impregnated with piperazine or triethylenediamine to remove iodine from nuclear waste effluent.

U.S. 3,355,317 to Keith et al. discloses the use of the oxides of cobalt, copper, zinc, iron and molybdenum on activated carbon to remove hydrogen cyanide from tobacco smoke.

U.S. 2,920,050 and U.S. 2,920,051, both to Blacet et al. describe the preparation of whetlerite type filters which include copper, chromium, silver and molybdenum impregnants.

In addition to the foregoing prior art patents, the comprehensive 1946 Government study entitled "Military Problems With Aerosols and Nonpersistent Gases", Volume I, sponsored by the Office of Scientific Research and Development (OSRD), describes the use of activated charcoal impregnated with various agents for removing noxious gases. Such as principally for gas masks devices.

Authored by Grabenstetter et al., Chapter 4 of the 1946 OSRD reports describing the use of copper, silver, chromium and molybdenum or vanadium impregnants on activated carbon to remove hydrogen cyanide and cyanogen chloride. Numerous organic base impregnations of charcoal are disclosed, including amines such as diethylene triamine and others.

U.S. 4,531,953 to Groose et al discloses the use of ASC whetlerite impregnated with triethylenediamine suitable for removing cyanogen chloride from a gaseous mixture.

G.B. 2,187,725 to Alder et al discloses an absorbent material suitable for removing toxic gases from a gaseous mixture, comprising an activated carbon having impregnated thereon at least one transition metal salt of a non-chelating carboxylic acid. Such material may also additionally contain triethylenediamine.

According to the present invention there is provided a method for removing cyanogen chloride from an air stream containing cyanogen chloride using an activated carbon or charcoal-containing filter, characterised in that said activated carbon or charcoal does not contain a transition metal salt of a non-chelating carboxylic acid nor chromium, but does contain triethylenediamine as a replacement for chromium in an amount for effectively removing cyanogen chloride.

The present invention is particularly directed to the use of a whetlerite type sorbent which avoids the use of a carcinogenic chromium component. Activated carbon or charcoal that has been impregnated with triethylenediamine as a replacement for chromium has been found to be particularly effective for gas masks for removing cyanogen chloride and without the need for chromium. The activated carbon or charcoal also may be impregnated with copper and/or silver for removal of additional toxic gases or vapors.

Another aspect of the present invention is a method for removing cyanogen chloride from an air stream using a whetlerite type filter material which comprises activated carbon or charcoal that has been impregnated with aqueous solutions of the soluble salts of copper and silver (type AS), and which additionally contains triethylenediamine (TEDA) as a replacement for chromium. Experiments have been performed to determine suitable impregnation methods and loading levels of TEDA as a replacement for chromium. Loadings of 4-6% TEDA (by weight) have been shown to yield a filter which meets U.S. Military specifications for cyanogen chloride removal, even when compared against the conventional chromium impregnated carbon or charcoal (type ASC). Performance of the TEDA impregnated filter after "aging" far exceeds that of chromium based material.

The respective amounts of these components present in the impregnating solution are typically as follows:

Copper: up to 20 weight percent, preferably 7 to 15%, for example, as copper carbonate;

Silver: up to 0.5 weight percent, preferably 0.03 to 0.1, added for example as silver nitrate;

Triethylenediamine: 1.0 to 7.5 weight percent, preferably 2 to 6%.

Also in accordance with the present invention there is provided a gas mask device for removing cyanogen chloride gas from an air stream containing cyanogen chloride comprising a housing means containing activated carbon or charcoal, characterised in that said activated carbon or charcoal does not contain a transition metal salt of a non-chelating carboxylic acid nor chromium but does contain triethylenediamine as a replacement for chromium in an amount for effectively removing cyanogen chloride.

The present invention also relates to type AS whetlerite charcoal impregnated with triethylenediamine as a replacement for chromium in an amount effective for removing cyanogen chloride from an air stream containing cyanogen chloride a transistion metal salt of a non-chelating carboxylic acid.

The precursor filter material used in the present invention can be conventionally prepared in accordance with the procedures described by the two patents to Blacet et al. (U.S. 2,920,050 and 2,920,051). Thus, activated carbon particles are impregnated with solutions of the respective salts of copper and silver, followed by drying. Typical procedures and formulations for copper and silver impregnations are also described by Grabenstetter et al. in the 1946 OSRD report, supra, which is incorporated herein by reference. Drying of the initially impregnated carbon can be carried out in a fluidised bed, oven, or air stream at temperatures of about 93° to 315°C (200° to 600°F)preferably about 177° to 232°C (350° to 450°F). It is also desirable first to dry the initially impregnated carbon at a lower temperature of 107° to 135°C (225° - 275°F) followed by heat treatment at a higher range of 177° to 315°C (350° to 600°F). Thereafter, impregnation with TEDA can be carried out by adding an aqueous solution of the amine to the metal impregnated carbon, followed by drying at about 65° to 149°C (150°F to 300°F).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following description and examples provide details of the manner in which the embodiments of the present invention can be made and used to effectively remove cyanogen chloride from air without the presence of chromium. The examples shown are based on actual experimental work. While exemplary of the present invention, the examples should not be construed as specifically limiting the invention and such variations which would be within the purview of one skilled in the art are to be considered to fall within the scope of the invention.

Preparation of Impregnated Samples

Samples were prepared in which triethylenediamine (TEDA) was added to a whetlerite type filter material impregnated with copper and silver (type AS). The first set of AS/TEDA samples which were prepared (samples 83-003 through 83-014) were made from various precursor carbons and employed a

range of TEDA loadings to test the effects of these variables on cyanogen chloride protection. The steps involved in sequentially impregnating, drying and heat-treating the base material, and impregnating with TEDA are described below. The resulting fully impregnated carbon samples, were used to evaluate the effect of TEDA on cyanogen chloride life in the absence of chromium. Activated carbons were impregnated with a solution containing soluble copper and silver salts. The carbon contained about 7.5% copper and 0.05% silver. The product was dried in a forced air oven at 149 ° to 188 °C (300 ° - 370 °F).

The dried AS carbon then was impregnated with TEDA by adding an aqueous solution of the amine to give a series of products with TEDA loadings ranging from 1.5% to 7.5% (by weight).

Some samples were prepared by spraying an aqueous TEDA solution onto the carbon and others were made by soaking it with the TEDA solution. In all TEDA impregnations, the final product was dried at 110 °C for 3 hours.

A second set of AS/TEDA samples, including sample numbers 83-102 through 83-112, was prepared using the fluid bed processing conditions shown in TABLE 1 for heat treatment of the AS precursor. The fluid bed method of heat treatment provides improved ammonia desorption characteristics compared to the treatment in the forced air oven.

TABLE 1

Fluid Bed Processing Conditions For Heating Type AS Material	
Fluid-bed vessel diameter cm (inches)	10.2 (4.0)
Fluidizing velocity m/s (ft/sec)	12.6 (2.0)
Test mode	Batch
Residence Time (min.)	5 and 10
Atmosphere	Air and simulated flue gas
Temperatures °C (°F)	135 and 191 (275 and 375)

As shown in TABLE 2, samples 003-007 were based on carbon impregnated with the AS solution and supplemented with TEDA applied by spraying amounts ranging from 1.5% to 7.5%. The precursor type AS whetlerites were conventionally prepared using the forced air oven. Maximum benefit of TEDA is obtained for amounts of 4.5% and greater. At such loadings the cyanogen chloride life of original samples appears to be dependably above 40 minutes (min) and aging had no detrimental effect.

TABLE 2

Cyanogen Chloride Life Comparison for Type AS Carbons Impregnated With TEDA				
Sample No. 83-( )	%TEDA	Method	Original Life (Min)	Aged Life (Min)
003	1.5%	Spray	37.1	27.5
004	3.0%	Spray	40.9	34.4
005	4.5%	Spray	40.7	58.1
006	6.0%	Spray	48.2	41.0
007	7.5%	Spray	42.1	44.7
008	3.0%	Soak	33.2	29.1
009	6.0%	Soak	38.8	41.1
010	6.0%	Spray	40.9	35.0
011	6.0%	Spray	40.0	35.0
012			nil	nil
013			nil	nil

Results for a second set of samples, for which the type AS whetlerite precursor was made using fluid bed heat treatment, are shown in TABLE 3. These products were all made with a 6% TEDA loading. A number of different heat treatment temperatures were used ranging from 135 ° to 427 °C (275 ° to 800 °F), and effects of both air and flue gas as purge gases were tested.

For the AS/TEDA products the average original cyanogen chloride life for 8 samples was 42.9 min. After aging, the cyanogen chloride life was 39.8 min.

TABLE 3

Cyanogen Chloride Life Of Chromium-Free Products Containing 6% TEDA					
Sample No. (83-( )	Sample	Atm	Temp.	Cyanogen Chloride Life (Min.)	
				Org. Avg.	Aged Avg.
102	AS/TEDA	FG**	275°F	45.0	38.3
103			300°	41.9	36.4
104			350°	40.9	34.2
105			400	39.6	39.7
106			500	40.7	39.4
107			650	44.9	50.5
108			800	48.1	39.6
109		Air	350	42.3	40.2
				Avg. 42.9	Avg. 39.8
110		Air	350	36.8	35.5
				Avg. 38.8	Avg. 35.5
111		Air	350	30.4	29.0
112		FG	350	29.2	32.0
				Avg. 29.8	Avg. 30.5

** Flue Gas

From the foregoing, it will be seen that the use of TEDA as an impregnating agent with Type AS whetlerites yields improved cyanogen chloride protection. Thus, TEDA can replace chromium and eliminate the various problems associated with the use of this metal.

Although only preferred embodiments are specifically illustrated and described herein, it will be appreciated that many modifications and variations of the present invention are possible in light of the above teachings and within the purview of the appended claims without departing from the spirit and intended scope of the invention.

It will also be appreciated that the experiments conducted and reported herein involve Type AS whetlerites since this is the material most suitable for use for protection against a variety of gases. However, it should be understood that the use of TEDA as a chromium substitute with charcoals other than Type AS is also contemplated since the effectiveness of TEDA alone has been amply demonstrated for removal of cyanogen chloride from air streams.

Claims

1. A method for removing cyanogen chloride from an air stream containing cyanogen chloride using an activated carbon or charcoal-containing filter, characterised in that said activated carbon or charcoal does not contain a transition metal salt of a non-chelating carboxylic acid nor chromium, but does contain triethylenediamine as a replacement for chromium in an amount for effectively removing cyanogen chloride.

2. A method as claimed in claim 1, characterised in that said triethylenediamine is present in an amount ranging from 1.0 to 7.5 weight %.

3. A method as claimed in claim 2, characterised in that said triethylenediamine is present in an amount ranging from 4 to 6 weight %.

4. A method as claimed in claim 1, 2 or 3, characterised in that said activated carbon or charcoal further includes up to 20 weight percent copper.

5. A method as claimed in claim 1, 2 or 3, characterised in that said carbon further includes up to 0.5 weight percent silver.

6. A method as claimed in claim 1, 2, or 3, characterised in that said carbon further includes copper and silver.

7. A method as claimed in claim 6, characterised in that said carbon further includes from 5 to 20 weight percent copper and from 0.03 to 0.1 weight percent silver.

8. A gas mask device for removing cyanogen chloride gas from an air stream containing cyanogen chloride comprising a housing means containing activated carbon or charcoal, characterised in that said activated carbon or charcoal does not contain a transition metal salt of a non-chelating carboxylic acid nor contain chromium, but does contain triethylenediamine as a replacement for chromium in an amount for effectively removing cyanogen chloride.

9. A device as claimed in claim 8, characterised in that said activated carbon or charcoal further includes up to 20 weight percent copper.

10. A device as claimed in claim 9, characterised in that the copper content is from 5 to 20 weight percent.

11. A device as claimed in claim 8, characterised in that said activated carbon or charcoal further includes up to 0.5 weight percent silver.

12. A device as claimed in claim 11, characterised in that the silver content is from 0.03 to 0.1 weight percent.

13. A device as claimed in claim 8, characterised in that said activated carbon or charcoal further includes copper and silver.

14. A device as claimed in any one of claims 8 to 13, characterised in that the triethylenediamine content is from 1.0 to 7.5 weight percent.

15. A device as claimed in claim 14, characterised in that the triethylenediamine content is from 2 to 6 weight percent.

16. Type AS whetlerite charcoal impregnated with triethylenediamine as a replacement for chromium in an amount effective for removing cyanogen chloride from an air stream containing cyanogen chloride, but not including a transition metal salt of a non-chelating carboxylic acid.

Patentansprüche

1. Verfahren zum Entfernen von Chlorcyan aus einem Chlorcyan enthaltenden Luftstrom durch Verwendung eines Aktivkohle oder Holzkohle enthaltenden Filters.
dadurch gekennzeichnet,
daß die Aktivkohle oder Holzkohle weder ein Übergangsmetallsalz einer nichtchelatbildenden Karbonsäure noch Chrom aber Triäthylendiamin als Ersatz für Chrom in einer Menge enthält, die wirksam Chlorcyan entzieht.

2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß das Triäthylendiamin in einer Menge im Bereich von 1,0 bis 7,5 Gewichtsprozent vorhanden ist.

3. Verfahren nach Anspruch 2,
dadurch gekennzeichnet,
daß das Triäthylendiamin in einer Menge im Bereich von 4 bis 6 Gewichtsprozent vorhanden ist.

4. Verfahren nach Anspruch 1, 2 oder 3,
dadurch gekennzeichnet,
daß die Aktivkohle oder Holzkohle des weiteren bis zu 20 Gewichtsprozent Kupfer enthält.

5. Verfahren nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet**, daß die Kohle weiterhin bis zu 0,5 Gewichtsprozent Silber enthält.

6. Verfahren nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet**, daß die Kohle weiterhin Kupfer und Silber enthält.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet**, daß die Kohle weiterhin Kupfer im Bereich von 5 bis 20 Gewichtsprozent Kupfer und Silber im Bereich von 0,03 bis 0,1 Gewichtsprozent enthält.

8. Gasmaskenvorrichtung zum Entfernen von Chlorcyangas aus einem Chlorcyan enthaltenden Luftstrom aufweisend ein Gehäuse mit Aktivkohle oder Holzkohle, **dadurch gekennzeichnet**, daß die Aktivkohle oder Holzkohle weder ein Übergangsmetallsalz einer nichtchelatbildenden Karbonsäure noch Chrom, jedoch Triäthylendiamin als Ersatz für Chrom in einer Menge enthält, die wirksam Chlorcyan entzieht.

9. Vorrichtung nach Anspruch 8, **dadurch gekennzeichnet**, daß die Aktivkohle oder Holzkohle des weiteren bis zu 20 Gewichtsprozent Kupfer enthält.

10. Vorrichtung nach Anspruch 9, **dadurch gekennzeichnet**, daß der Kupfergehalt im Bereich von 5 bis 20 Gewichtsprozent liegt.

11. Vorrichtung nach Anspruch 8, **dadurch gekennzeichnet**, daß die Aktivkohle oder Holzkohle des weiteren bis zu 0,5 Gewichtsprozent Silber enthält.

12. Vorrichtung nach Anspruch 11, **dadurch gekennzeichnet**, daß der Silbergehalt im Bereich von 0,03 bis 0,1 Gewichtsprozent liegt.

13. Vorrichtung nach Anspruch 8, **dadurch gekennzeichnet**, daß die Aktivkohle oder Holzkohle des weiteren Kupfer und Silber enthält.

14. Vorrichtung nach irgendeinem der Ansprüche 8 bis 13, **dadurch gekennzeichnet**, daß der Gehalt an Triäthylendiamin im Bereich von 1,0 bis 7,5 Gewichtsprozent liegt.

15. Vorrichtung nach Anspruch 14, **dadurch gekennzeichnet**, daß der Gehalt an Triäthylendiamin im Bereich von 2 bis 5 Gewichtsprozent liegt.

16. Typ AS Whetlerit-Holzkohle, die mit Triäthylendiamin als Ersatz für Chrom in einer Menge, die für die Entfernung von Chlorcyan aus einem Chlorcyan enthaltenden Luftstrom wirksam ist, imprägniert ist, aber kein Übergangsmetallsalz einer nichtchelatbildenden Karbonsäure enthält.

Revendications

1. Procédé pour extraire du chlorure de cyanogène d'un courant d'air contenant du chlorure de cyanogène, par utilisation d'un filtre contenant du charbon activé ou du charbon de bois, caractérisé en ce que le charbon activé ou le charbon d bois ne contient ni sel d'un métal de transition d'un acide carboxylique non chélatant, ni du chrome, mais contient en fait de la triéthylènediamine en remplace-

ment du chrome en une quantité suffisante pour extraire d'une manière efficace le chlorure de cyanogène.

2. Procédé selon la revendication 1, caractérisé en ce que la triéthylènediamine est présente en une quantité comprise entre 1,0 et 7,5 % en poids.

3. Procédé selon la revendication 2, caractérisé en ce que la triéthylènediamine est présent en une quantité comprise entre 4 et 6 % en poids.

4. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que le charbon activé ou le charbon de bois contient en outre, jusqu'à 20 % en poids de cuivre.

5. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que le charbon contient en outre jusqu'à 0,5 % en poids d'argent.

6. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que le charbon contient en outre du cuivre et de l'argent.

7. Procédé selon la revendication 6, caractérisé en ce que le charbon contient en outre de 5 à 20 % en poids de cuivre et de 0,03 à 0,1 % en poids d'argent.

8. Dispositif de masque à gaz pour éliminer le chlorure de cyanogène gazeux se trouvait dans un courant d'air contenant du chlorure de cyanogène, qui comprend un moyen de boîtier contenant du charbon activé ou du charbon de bois, caractérisé en ce que le charbon activé ou le charbon de bois ne contient ni sel d'un métal de transition d'un oxyde carboxylique non chélatant, ni chrome, mais contient en fait de la triéthylènediamine, en remplacement du chrome, en une quantité suffisante pour extraire d'une manière efficace le chlorure de cyanogène.

9. Dispositif selon la revendication 8, caractérisé en ce que le charbon activé ou le charbon de bois contient en outre jusqu'à 20 % en poids de cuivre.

10. Dispositif selon la revendication 9, caractérisé en ce que la teneur en cuivre est de 5 à 20 % en poids.

11. Dispositif selon la revendication 8, caractérisé en ce que le charbon activé ou le charbon de bois contient en outre jusqu'à 0,5 % en poids d'argent.

12. Dispositif selon la revendication 8, caractérisé en ce que la teneur en argent est de 0,03 à 0,1 % en poids.

13. Dispositif selon la revendication 8, caractérisé en ce que le charbon activé ou le charbon de bois contient en outre du cuivre et de l'argent.

14. Dispositif selon l'une quelconque des revendications 8 à 13, caractérisé en ce que la teneur en triéthylènediamine est de 1,0 à 7,5 % en poids.

15. Dispositif selon la revendication 14, caractérisé en ce que la teneur en triéthylènediamine est de 2 à 6 % en poids.

16. Charbon de bois, à base de whetlerite, type AS, imprégné de triéthylènediamine en remplacement du chrome en une quantité suffisante pour extraire du chlorure de cyanogène à partir d'un courant d'air contenant du chlorure de cyanogène, mais ne contenant aucun sel d'un métal de transition d'un acide carboxylique non chélatant.